

II. REMARKS

A. Introductory Remarks

Reconsideration and allowance of this application is earnestly requested. Claims 1-17 are currently pending. Claims 1, 2, 4, 5, 6, 7, 9 and 12 are amended by this Amendment, and claims 3 and 11 have been canceled. New claims 18, 19 and 20 have been added. No new matter has been added by these amendments.

B. Rejection of Claims 1-3 Under 35 U.S.C. §103

The Office Action rejected claims 1 and 12 as allegedly unpatentable over U.S. Patent Application No. 2003/0181142 A1 (“De Rege”). In light of the amendment made to independent claim 1 and 12, Applicants traverse this rejection.

With respect to claims 1 and 12, the Office Action asserts that De Rege discloses 31 specifically named sulfonic acid compounds and at least 2 of these, 3-amino-4-hydroxybenzenesulfonic acid and 2-formylbenzenesulfonic acid, would meet the limitation of part B of claim 1. Further, the Office Action asserts that both these compounds are organosulfonic acid oxidizer having one ring structure comprising carbon (the benzene ring), a sulfonate moiety substituted onto a carbon atom in the ring structure (the sulfonic acid group at position 1 on the benzene ring), and a polar moiety substituted on the ring on a meta position from the sulfonate moiety (the amino group is polar and is in the ortho position 2 on the ring). See Office Action on page 2-3.

Applicants have amended independent method claims 1 and 12 to incorporate the limitations of claim 3 with the exception of the recitation of an “amino moiety.” Accordingly, part B of claims 1 and 12 now additionally recite, “said polar moiety substituted onto the ring in the “ortho” or “meta” position from the sulfonate moiety comprises a sulfonate moiety, a sulfate moiety, a nitro moiety, a nitroso moiety, a hydroxyl moiety, a carboxylate moiety, a sulfamic acid moiety, or a methoxy moiety.” Applicant submits that De Rege does not teach or suggest the organosulfonic acid oxidizers of amended claims 1 and 12 that have polar moieties substituted on the “ortho” and “meta” position on the benzene ring of the organosulfonic acid

oxidizers. De Rege provides a list of benzenesulfonic acid compounds that have “ortho”, “meta”, or “para” substituted benzene rings, which may comprise both polar and non-polar groups. Accordingly, given such the large number of compounds and the various types of organosulfonic acids disclosed in De Rege, one skilled in the art would not be motivated to modify the teachings of DeRege to generate a organosulfonic acid oxidizer substituted with one of the specific polar groups on the “ortho” and “meta” positions as recited in amended claims 1 and 12. For the foregoing reasons Applicants requests withdrawal of this rejection as to claims 1 and 12 and the claims that depend therefrom.

C. The Rejection of Claims 6-7 Under 35 U.S.C. §103 (a)

Claims 2-8, 10-11 have been rejected as obvious under 35 U.S.C. §103 (a) over De Rege in view of U.S. Patent No. 6,899,596 (“Antonell”). Applicants traverse this rejection.

First, claims 2-8, and 10-11 depend from independent claim 1. As discussed above, De Rege fails to teach or suggest each and every limitation of amended claim 1. Accordingly, on this basis alone, Applicants request withdrawal of this rejection as to dependent claims 2-8, and 10-11.

Second, neither DeRege nor Antonell teach or suggest a organosulfonic acid oxidizer having an electrochemical oxidation potential greater than 0.7V as recited in claims 2 and 10. Antonell teaches a CMP polishing process using a chemically active slurry having a polarity selected to affect the relative oxidation rates of respective crystalline places of a polycrystalline surface being polished. See abstract. The slurry for controlling material removal rates comprises a primary carrier constituent, an oxidizing constituent, and a polarity-influencing constituent. See col. 2 lines 4-9. Further, Antonell teaches that the polarity-influencing constituent may be a material having a polarity less than that of water, for example, a constituent having a dipole moment less than 1.8, which may be benzene. See col. 5 lines 10-13. The selected solute will equilibrate the oxidation rates of the different orientation phases. See col. 4 lines 25-27. Basically, Antonell teaches that benzene or carbon tetrachloride with a dipole moment polarity of zero may be mixed with other chemicals to produce a desired polarity value to control the polarity of the slurry and affect the oxidation rates. See col. 4 lines 20-27.

Applicant submits that the dipole moment of various solvents disclosed in Antonell is not related to the oxidation potential of the benzenesulfonic compound. Oxidation rate as disclosed in Antonell is also not the same thing as oxidation potential. Oxidation potential is a thermodynamic parameter related to the thermodynamic free energy as follows: $\Delta G = n F \Delta E^\circ$. See P. W. Atkins, "Physical Chemistry", 4th Edition on page 261. In contrast, the dipole moment is a physical parameter derived from the product of the charge times the distance ($\Delta\mu = e \times R$). See P. W. Atkins, "Physical Chemistry", 4th Edition on page 645. Antonell does not teach or suggest a relationship between the dipole moment of the solvents to the thermodynamic electrochemical potential (oxidation potential). Thus, one of skill in the art would not be motivated to modify the teachings of DeRege based on the teaching of Antonell to provide an oxidation potential of 0.7V as recited in claims 2 and 10.

Even if such a relationship exists between the dipole moment and the oxidation potential, Antonell prefers lower dipole moments not higher dipole moments. Claims 2 and 10 recite that the organosulfonic acid has an electrochemical oxidation potential greater than 0.7V. With respect to polar-moiety-substituted benzenes, the lowest dipole moment is found in para-substituted benzenes not the "ortho" and the "meta" substituted positions. Dipole moment is higher in the "ortho" and "meta" position due to the asymmetrical distribution of charge in these positions. Thus, Antonell fails to provide the requisite motivation to alter DeRege's teachings to arrive at the invention of claims 2 and 10, and Applicant requests withdrawal of this rejection as to claims 2 and 10 and as to the corresponding dependent claims 3-8 and 11.

D. Allowable Subject Matter

Applicant acknowledges with appreciation the allowance of claim 14-16.

E. New Claims 18, 19 and 20

New claims 18, 19 and 20 have been added by this Amendment. None of the references cited above, alone or in combination, teach or suggest the limitations of these claims. These claims further recite the specific type of polar organosulfonic acid oxidizer (3-nitrobenzenesulfonic acid) of claims 1 and 12. New claim 20 recites a 3-amino benzenesulfonic acid as the organosulfonic acid oxidizer, which is not disclosed or suggested by DeRege.

DeRege discloses 3-amino-4-hydroxybenzenesulfonic acid, which contains two polar moieties unlike the benzene sulfonic acid of claim 20 which contains only one polar moiety. In view of these distinctions, Applicants submit that all these claims are in condition for allowance.


III. Request for Allowance

In view of the arguments presented above, all pending claims are now thought to be in condition for allowance, an indication of which is solicited. In the event that any issues remain outstanding, Applicants would appreciate the courtesy of a telephone call to the undersigned counsel to resolve such issues in an expeditious manner so as to place this application in condition for allowance.

No additional fees are believed due, other than the separately filed one-month extension fee. However, if any additional fees are determined to be due, the Commissioner is hereby authorized to charge these fees to the Morgan, Lewis & Bockius deposit account no. 50-0310.

Respectfully submitted,

MORGAN LEWIS & BOCKIUS LLP

By 

Laba Karki, Ph.D. Reg. No. 55,317
Attorney of Record

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Customer No. 09629
1111 Pennsylvania Avenue, N.W.
Washington, D.C. 20004
Phone: (202) 739-3000
Facsimile: (202) 739-3001
Direct: (202) 739-5590

PHYSICAL CHEMISTRY

FOURTH EDITION

P.W. ATKINS



W. H. Freeman and Company
New York

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This work is infinitesimal, and the composition of the system is virtually constant when it occurs.

Suppose that when the reaction advances by an amount $d\xi$, an amount $\nu d\xi$ of electrons must travel from the anode to the cathode. The total charge transported between the electrodes when this occurs is $-eN_A d\xi$ (because $\nu d\xi$ is the amount of electrons transferred and the charge of an electron is $-e$). The product of e and N_A is called the **Faraday constant** F :

$$F = 96.485 \text{ kC mol}^{-1}$$

F is the magnitude of the charge per mole of electrons. Hence, the total charge transported is $-\nu F d\xi$.

The work done when an infinitesimal charge $-\nu F d\xi$ travels from the anode to the cathode is equal to the product of the charge and the potential difference E (Table 2.1):

$$dw_e = -\nu F d\xi \times E$$

When we equate this work to the expression for dG , the advancement $d\xi$ cancels, and we find

$$-\nu F E = \Delta G_r \quad (10a)$$

Therefore, knowing the reaction Gibbs function at a specified composition, we can state the zero-current cell potential at that composition. Note that a negative reaction Gibbs function, corresponding to a spontaneous cell reaction, corresponds to a positive zero-current cell potential.

Example 10.8: Estimating a cell potential

Estimate the cell potential that can be expected for a typical cell reaction.

Answer. We have calculated a number of reaction Gibbs functions in previous chapters and sections of this chapter, and have seen that they are of the order of -100 kJ mol^{-1} . Therefore, taking ν as 1, we can expect a typical cell potential to be of the order of

$$E \approx -\frac{(-100 \times 10^3 \text{ J mol}^{-1})}{96 \times 10^3 \text{ C mol}^{-1}} = 1 \text{ V}$$

since $1 \text{ J} = 1 \text{ C V}$.

Exercise. Estimate the zero-current cell potential for a cell in which the reaction is $\text{H}^+(\text{aq}, 0.020 \text{ mol kg}^{-1}) \rightarrow \text{H}^+(\text{aq}, 0.010 \text{ mol kg}^{-1})$ at 25°C . $[E = (RT/F) \ln 2.0 = 18 \text{ mV}]$

The Nernst equation

We can go on to relate the zero-current cell potential to the activities of the participants in the cell reaction. We know from eqn 4 in Section 9.2 that the reaction Gibbs function is related to the composition by

$$\Delta G_r = \Delta G^\ominus + RT \ln Q \quad Q = \prod_j a_j^{\nu_j}$$

Therefore,

$$E = -\frac{\Delta G^\ominus}{\nu F} - \frac{RT}{\nu F} \ln Q$$

The first term on the right of this equation is called the **standard cell potential** and denoted E^\ominus :

$$- \nu F E^\ominus = \Delta G^\ominus \quad (10b)$$

It is the standard reaction Gibbs function of the reaction expressed as a potential (in volts). It follows that

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad (11)$$

This is the **Nernst equation** for the zero-current cell potential at any cell composition. Since $RT/F = 25.7 \text{ mV}$ at 25°C , a practical form of eqn 11 is

$$E = E^\ominus - \frac{25.7 \text{ mV}}{\nu} \ln Q$$

Hence, for a reaction in which $\nu = 1$, if Q is increased by a factor of 10, the cell potential increases by 59.2 mV .

Example 10.9: Using the Nernst equation to calculate a cell potential

Calculate the zero-current cell potential of a Daniell cell at 25°C in which the molality of copper(II) sulphate is 1.0 mol kg^{-1} and that of zinc sulphate is 3.0 mol kg^{-1} .

Answer. The cell reaction (the reduction of Cu^{2+} ions by zinc) is



We need the mean activity coefficients in each of the solutions. Since they are both 2:2 electrolytes, the ionic strength is $4m$ (Table 10.3), and by the Debye-Hückel limiting law (eqn 5),

$$\lg \gamma_{\pm} = \frac{-0.509}{(\text{mol kg}^{-1})^{1/2}} \times 4 \times (4m)^{1/2}$$

which evaluates to 0.74 for the copper(II) sulphate and 0.60 for the zinc sulphate. Hence,

$$Q = \frac{0.60 \times 0.0030 \text{ mol kg}^{-1}}{0.74 \times 0.0010 \text{ mol kg}^{-1}} = 2.43$$

The standard reaction Gibbs function is calculated from the standard Gibbs functions of formation:

$$\begin{aligned} \Delta G^\ominus &= \Delta G_f^\ominus(\text{Zn}^{2+}(\text{aq})) - \Delta G_f^\ominus(\text{Cu}^{2+}(\text{aq})) \\ &= -147.1 - (-65.6) \text{ kJ mol}^{-1} = -212.7 \text{ kJ mol}^{-1} \end{aligned}$$

Hence we find

$$E^\ominus = -\frac{(-212.7 \text{ kJ mol}^{-1})}{2 \times 96.485 \text{ kC mol}^{-1}} = +1.102 \text{ V}$$

Therefore, from the Nernst equation,

$$E = 1.102 \text{ V} - (25.7 \times 10^{-3} \text{ V}) \ln 2.43 = 1.08 \text{ V}$$

Exercise. Calculate the zero-current potential of the cell $\text{Pt} | \text{H}_2(\text{g}, 2.0 \text{ bar}) | \text{HCl}(\text{aq}, 0.10 \text{ mol kg}^{-1}) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}(\text{l})$ at 25°C . Take activity coefficients from Table 10.4. $[0.400 \text{ V}]$

The electric and magnetic properties of molecules

Check-list of key ideas

1. The definition of the *electric dipole moment* and the approximate additivity of dipole moments in polyatomic molecules (Section 22.1).
2. The *polarizability* and *polarizability volume* of a molecule and its contribution to the *polarization* of a medium (Section 22.1).
3. The *polarization* of a medium as the mean dipole moment per unit volume (Section 22.1).
4. The variation of the polarizability with frequency and the *orientation, distortion, and electronic contributions* (Section 22.1).
5. The *Debye equation* for the contribution of the permanent dipole moment and the polarizability to the polarization (eqn 5a).
6. The *Clausius-Mossotti equation* for the polarization when the permanent dipole does not contribute (eqn 5b).
7. The *molar polarization* (eqn 6a) and the *molar refractivity* (eqn 9) of a substance.
8. The *refractive index* of a substance, its *dispersion* (Section 22.2), and its calculation from molecular contributions (eqn 10).
9. Circular birefringence, the origin of *optical activity*, and *optical rotatory dispersion* (Section 22.2).
10. The *circular dichroism* of chiral molecules (Section 22.2).
11. The origin of *van der Waals forces* between molecules (Section 22.3).
12. The *potential energy* of interaction between a charge and an electric dipole (eqn 11), between two dipoles (eqn 12), and between higher *multipoles*.
13. The *electric field* developed by an electric dipole (eqn 13).
14. The average *dipole/dipole interaction* of rotating polar molecules (eqn 16).
15. The *dipole/induced-dipole interaction* between a polar molecule and a polarizable molecule (eqn 17).
16. The *induced-dipole/induced-dipole interaction* between molecules and the *London dispersion interaction* (eqn 18).
17. The contribution of *three-body interactions* and the *Axilrod-Teller formula* (Section 22.3).

Electric properties

22.1 Permanent and induced electric dipole moments

22.2 Refractive index

Intermolecular forces

22.3 Interactions between dipoles

22.4 Repulsive and total interactions

22.5 Molecular interactions in beams

Gases and liquids

22.6 Gas imperfections

22.7 The structures of liquids

22.8 Liquid crystals

22.9 Molecular motion in liquids

Magnetic properties

22.10 Magnetic susceptibility

22.11 The permanent magnetic moment

22.12 Induced magnetic moments

Further information: the Langevin function

Further reading

Exercises

Problems

18. The *hard-sphere potential* and the *Lennard-Jones potential* (eqn 20).

19. The study of molecular interactions in *molecular beams* and the significance of the *differential scattering cross-section* and the *impact parameter* (Section 22.5).

20. The phenomena of *glory scattering* and *rainbow scattering* (Section 22.5).

21. The contribution of the intermolecular potential to the *virial coefficients* of a real gas and its calculation in terms of the *configuration integral* and the *Mayer f -function* (eqn 22).

22. The description of liquids in terms of the *pair distribution function* and calculations using the *Monte Carlo method* and *molecular dynamics* (Section 22.7).

23. The *mesophase* and the classification of *liquid crystals* (Section 22.8).

24. Molecular motion in liquids and the temperature dependence of the *viscosity* (Section 22.9).

25. The *magnetic susceptibility* of a substance and its classification as *paramagnetic* and *diamagnetic* (Section 22.10).

26. The *Curie Law* of magnetism (eqn 26).

27. The contribution of electron spin to the magnetic susceptibility and the transition to *ferromagnetic* and *antiferromagnetic* phases (Section 22.11).

28. The contribution of *induced magnetic moments* to the magnetic susceptibility and the origin of *temperature-independent paramagnetism* (Section 22.12).

In this chapter we examine some of the electric and magnetic properties of molecules and interpret them in terms of electronic structure. The properties we consider include the electric dipole moments and polarizabilities of molecules and some related properties that include refractive index, optical activity, and intermolecular forces. We also discuss the analogous magnetic properties, particularly the magnetizabilities and the magnetic susceptibilities of molecules.

Electric properties

An **electric dipole** consists of two charges q and $-q$ separated by a distance l , and is represented by a vector μ that points from the negative charge to the positive charge. The magnitude of this vector (1) is ql and is called the **electric dipole moment** μ . An electric dipole is represented by the arrow \leftrightarrow added to the Lewis structure for the molecule, with the $+$ marking the positive end, as in $\text{H}-\text{Cl}$ (the direction of \leftrightarrow is opposite to that of the

vector μ). Dipole moments are generally reported in debye D, where

$$1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$$

The debye is named after Peter Debye, a pioneer in the study of dipole moments of molecules. The dipole moment of a pair of charges e and $-e$ separated by 100 pm (1 Å) is $1.6 \times 10^{-29} \text{ C m}$, corresponding to 4.8 D. Dipole moments of small molecules are typically about 1 D.

22.1 Permanent and induced electric dipole moments

A **polar molecule** is a molecule with a permanent electric dipole moment that arises from the partial charges on atoms linked by polar bonds (Section 14.6). Non-polar molecules may acquire a dipole moment in an electric field on account of the distortion the field causes in their electronic distributions and nuclear positions. Similarly, polar molecules may have their existing dipole moments modified by the applied field.

Permanent and induced dipole moments are important in chemistry through their role in intermolecular forces (as we describe later) and in their contribution to the ability of a substance to act as a solvent for ionic solids. The latter ability stems from the fact that one end of a dipole may be coulombically attracted to an ion of opposite charge and hence contribute an exothermic term to the enthalpy of solution (Fig. 22.1).

The average electric dipole moment per unit volume of a sample is called its **polarization P**. The polarization of a fluid sample is zero in the absence of an applied field because the molecules adopt random orientations and the average dipole moment is zero. In the presence of a field the dipoles are partially aligned and there is an additional contribution from the dipole moment induced by the field. Hence, the polarization of a medium in the presence of an applied field is non-zero.

Polar molecules

We explained in Section 16.4 how the Stark effect can be used to measure electric dipole moments of molecules for which a rotational spectrum can be observed. When microwave spectroscopy cannot be used (because the sample is not volatile, decomposes, or consists of complex molecules), the dipole moment may be obtained by measurements on a liquid or solid bulk sample using a method that we explain later. In the following we refer to the sample as a **dielectric**, by which we mean a polarizable, non-conducting medium.

All heteronuclear diatomic molecules are polar, and typical values are 1.08 D for HCl and 0.42 for HI (Table 22.1). A very approximate relation between the dipole moment and the difference in electronegativities of the two atoms $\Delta\chi$ is

$$\mu/D = \Delta\chi$$

The more electronegative atom is normally the negative end of the dipole, but there are exceptions, particularly when antibonding orbitals are occupied.¹ Thus the dipole moment of CO is very small (0.12 D) but the

¹ We remarked in Chapter 14 that the major contribution to an antibonding orbital is made by the atomic orbitals of the less electronegative atom. Hence, if that orbital is occupied there may be so much electron density of the less electronegative atom that that atom has a partial negative charge.

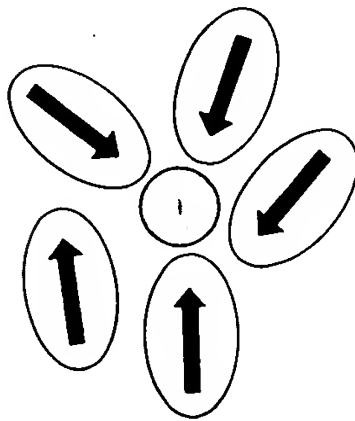


Fig. 22.1 An ion in a polar solvent is solvated as a result of its interaction with the dipoles of the solvent molecules.

Table 22.1. Dipole moments (μ) and polarizability volumes (α')

	μ/D	$\alpha'/(10^{-24} \text{ cm}^3)$
CCl_4	0	10.5
H_2	0	0.819
H_2O	1.85	1.48
HCl	1.08	2.63

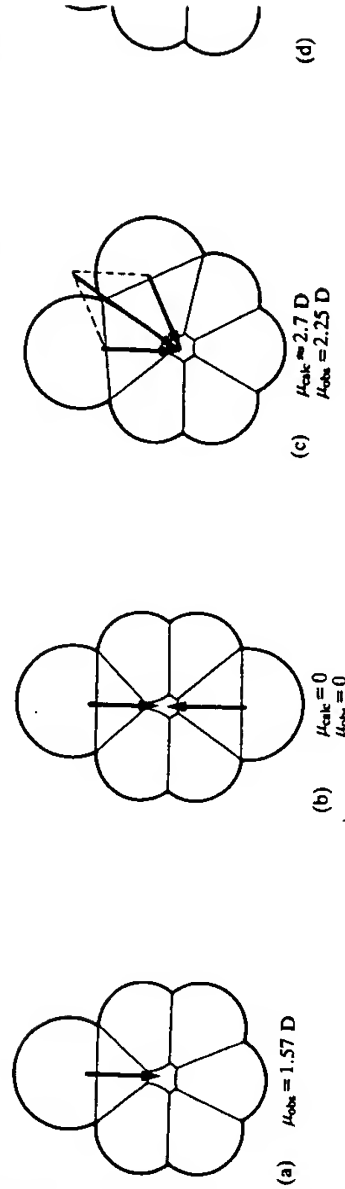


Fig. 22.2 The dipole moment of dichlorobenzene isomers, approximately by vectorial addition of the chlorobenzene dipole moment.

negative end of the dipole is on the C atom even though the O atom is more electronegative.

Whether or not a polyatomic molecule is polar depends on its symmetry. The criteria were discussed in Section 15.3, where we saw that a molecule is non-polar if it belongs to a D point group or to one of the cubic point groups. We also saw that the dipole moment of a molecule with a symmetry axis cannot lie perpendicular to that axis. The symmetry criterion is more important than the question of whether or not the atoms in the molecule are the same. Thus the homonuclear triatomic molecule O_3 (which is angular, with C_{2v} symmetry) is polar because the electron density on the central O atom is different from that on the two outer O atoms. The heteronuclear triatomic molecule CO_2 (which is linear, with $D_{\infty h}$ symmetry) is non-polar because the two bond dipoles point in opposite directions and cancel.

To some extent it is possible to resolve the dipole moment of a polyatomic molecule into contributions of various components (Fig. 22.2). Thus, p -dichlorobenzene is non-polar because of the cancellation of the two equal but opposing moments. o -Dichlorobenzene has a dipole moment which is approximately the resultant of two chlorobenzene dipole moments arranged at 60° . The technique of vector addition can be applied with fair success to other series of related molecules, and the resultant of two dipole moments that make an angle θ to each other (2) is

$$\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta)^{1/2}$$

If the two dipole moments are equal, this equation simplifies to

$$\mu = 2\mu_1 \cos \frac{1}{2}\theta$$

Induced dipole moments

As long as the applied electric field is not too strong the magnitude of the induced dipole moment μ^* is proportional to the field \mathcal{E} , and we write

$$\mu^* = \alpha \mathcal{E} \quad (1)$$

where the constant α is the **polarizability** of the molecule. When the field is strong (as in laser beams) the induced moment also depends on \mathcal{E}^2 and higher powers of the field. We then write

$$\mu^* = \alpha \mathcal{E} + \frac{1}{2} \beta \mathcal{E}^2 + \dots \quad (2)$$

where β is called the **hyperpolarizability**.